4. ALTERNATIVE WASTE FORM (CRYSTALLINE CERAMIC)

The screening process described in Appendix B identified crystalline ceramic as the primary alternative waste form to borosilicate glass. Crystalline ceramic is a generic term for a product of compatible mineral phases, formed at high temperatures. Two candidate waste forms, Synroc-D (a titanate-based ceramic) and tailored ceramic (an alumina/rare earth-based ceramic), are included in this term. In laboratory tests with simulated waste, the ceramic form has exhibited low leach rates, especially for uranium. Its mechanical and thermophysical properties are comparable to those of borosilicate glass, and its stability to damage from self-irradiation should be adequate based on studies with natural analogues. The process for immobilizing SRP high-level radioactive waste in crystalline ceramic is feasible, but is significantly more complex than the borosilicate glass process. The calculated environmental impacts resulting from production and disposal of the ceramic form are essentially the same as for the borosilicate glass waste form.

4.1 DESCRIPTION OF CERAMIC WASTE FORM

The crystalline ceramic waste form is a dense compact of compatible fine-grained oxide phases. Each of these phases serves as a "host" for one or more of the radioactive or inert elements present in SRP waste.[1] The ceramic form of primary interest for SRP waste immobilization is Synroc-D developed by LLNL[2] based on original work done by A. E. Ringwood at the Australian National University.[3] The expected phases in Synroc-D and the waste elements they contain are shown in Table 4-1.[1]

The Synroc-D form was designed specifically for SRP waste and utilizes titanate phases, zirconolite and perovskite, as the primary crystalline hosts for radionuclides. These phases are similar to natural minerals which have effectively retained radioactive elements for millions of years.[4] Synroc-D also includes other oxides, largely derived from the waste itself, such as spinels and nepheline, which accommodate large quantities of iron, aluminum, and sodium. The spinel phases would include essentially no radioactive elements, whereas nepheline and a related intergranular glassy phase contain cesium.[2]

TABLE 4-1

Typical Composition of Ceramic (Synroc-D) Phases with SRP Waste[1]

Mineral Phase	Approx. Phase Composition, wt %	Nominal Chemical Formula	Waste Elements*
Spinel	29	$FeAl_2O_4$-Fe_2TiO_4	Al, Fe, Mn, Ni
Perovskite	21	$CaTiO_3$	Sr, Ca, Ce, Nd, Act(III)**
Zirconolite	26	$CaZrTi_2O_7$	U, Ca, Act(IV)†
Nepheline and Glassy Si-Rich Phase	24	$NaAlSiO_4$	Na, Cs, Al, Si

* Important radionuclides are underlined.

** Trivalent actinides.

† Tetravalent actinides.

To promote the formation of these desirable phases, oxides or salts of titanium, zirconium, silicon, and calcium are added to the SRP waste feed before it is consolidated. Consolidation is accomplished at high temperatures and pressures to facilitate migration of chemical species to the favored phases and to densify the mixture. After consolidation, individual oxide grains are 1 to 2 micrometers in diameter or smaller.[2] For well-blended waste, about 65 wt %* sludge could be immobilized in Synroc-D with 35 wt % "tailoring" additives. The overall composition of Synroc-D containing well-blended SRP waste sludge is shown in Table 4-2. Unlike borosilicate glass, variations in waste composition could affect the ceramic's waste loading; for example, a large increase in Al_2O_3 content would result in a decrease in waste loading and radionuclide content.

* Without aluminum removal; waste loading on equivalent basis with borosilicate glass is ~52 wt %.

TABLE 4-2

Composition of Synroc-D and Waste Mixture Prior to Consolidation[1]

Constituent	Concentration in Mixture, wt % SRP Sludge	Additive
Fe_2O_3	18.9	--
Al_2O_3	17.9	--
MnO_2	4.3	--
U_3O_8	2.6	--
CaO	3.0	4.2
NiO	1.3	--
SiO_2	8.9	1.4
Na_2O	5.3	--
(Ca, Ba, Pb) SO_4	0.6	--
ThO_2	0.5	--
Others	2.1	--
TiO_2	--	20.1
ZrO_2	--	8.8
Total	65.5	34.5

The ceramic form, as currently envisioned, would be hot isostatically pressed in a carbon steel container. The reference ceramic canister would contain three such compacts enclosed in a stainless steel canister of about the same dimensions as the reference glass canister.[1] Major features of the canistered ceramic waste form are given in Table 4-3.

4.2 WASTE FORM PROPERTIES

In the following sections, leach resistance, important physical properties relating to mechanical and thermal stability, and radiation stability are summarized for the Synroc-D waste form. These properties were measured from Synroc-D samples containing simulated (nonradioactive) SRP waste.[2,3,5]

TABLE 4-3

Characteristics of Canistered Ceramic (Synroc-D) Waste Form

Characteristic	Synroc-D Ceramic[1]
Waste loading, wt %	65*
Waste form weight per canister, kg	2400
Total weight of waste canister, kg	3650
Waste form density, g/cm^3	4.0
Canister material	304L stainless steel
Canister dimensions	0.61 m in diameter 3.0 m in length 0.95-cm wall
Heat generation, W/canister (5-yr-old sludge plus 15-yr-old supernate)	1270
Heat generation after 1000 years, W/canister	<2
Radionuclide content, Ci/canister (5-yr-old sludge plus 15-yr-old supernate)	450,000
Radiation, R/hr at 1 m	~8700

* Without aluminum removal; waste loading on equivalent basis with borosilicate glass is ~52 wt %.

4.2.1 Leaching Properties

The Synroc-D waste form is expected to be very resistant to leaching by groundwaters in geologic repositories based on early leach test results.[2,6] Leaching data available on Synroc-D are primarily from MCC leach tests* for short time intervals (28 days or less) with simulated groundwater leachants.

Synroc-D leach rates for cesium, strontium, and uranium (generated in MCC-1 static leach tests) are summarized in Table 4-4. Leach rates of the short-lived fission products--primarily Cs-137 and Sr-90--would be important for accident

* Proposed standard waste form tests developed by the Materials Characterization Center of Pacific Northwest Laboratory.[7,8]

TABLE 4-4

Cesium, Strontium, and Uranium Leach Rates for Synroc-D*

Leachant	Leach Rate, $g/m^2 \cdot day$**		
	Cesium	Strontium	Uranium
Deionized Water	0.80	0.33	0.00008
Silicate Water	0.38	0.09	0.00028
Brine	<0.37	<0.10	0.0005

* Made with composite (blended) simulated waste.

** Values listed are average 28-day leach rates at 90°C from MCC-1 tests performed by LLNL, MCC, and SRL.[6]

conditions, which would expose the waste form to water during the operational and thermal periods of waste disposal. These periods include interim storage, transportation, and the first few hundred years in the repository. Leach resistance for uranium and other long-lived actinides is of interest for the entire geologic isolation period.

Synroc-D leach rates measured in short-term MCC tests are comparable to those of borosilicate glass for cesium, are higher for strontium, and are lower for uranium.[6] Other major results of leaching studies on Synroc-D include:[2,6]

- Leaching of the multi-phase Synroc-D ceramic is incongruent (that is, varies depending on element leached) because some phases retain the waste elements more strongly than other phases; for example, zirconolite retains uranium more effectively than nepheline and the intergranular glassy phase retain cesium.

- The effects of waste composition and leachant composition on leaching are relatively small; changes in leach rates from these effects are typically less than a factor of 5.

- The effect of flow rate is variable; however, at the lowest flow rate studied, which corresponds most closely to expected flow in a repository, leach rates are about the same as in static leach tests.

The long-term resistance to leaching of Synroc-D by groundwater is difficult to predict accurately from the short-term MCC leach tests because of the different durabilities of the Synroc phases and the lack of information on protective layer formation. Generally, the silica-rich phases (nepheline and the intergranular glassy phase), which contain cesium and some strontium, are least durable, while zirconolite (which contains uranium) is the most resistant to leaching. Release rates in a repository will depend upon interactions between the groundwater, waste form, other engineered barriers, and phases formed by precipitation of components released from the waste form.

4.2.2 Physical Properties

The Synroc-D form is a hard, high-strength ceramic with mechanical and thermophysical properties listed in Tables 4-5 and 4-6, respectively. These physical properties are, in general, similar to those of the borosilicate waste form. In particular, the quantity of respirable fines (<10-μm particles) generated in an impact test of 10 J/cm^3 energy density was only 0.16%, which is approximately equal to the fines fraction generated from borosilicate glass in similar tests.

The effects of self-irradiation over long isolation periods on the properties of the Synroc-D waste form are not as well characterized as for borosilicate glass. However, evidence from studies of natural zirconolite and perovskite phases containing uranium and thorium indicate that Synroc should remain a durable host for the actinides for at least 10^6 years of geologic isolation.[2,4] The major damage mechanism in Synroc would be atom displacement caused by alpha decay, which could produce loss of crystal structure (metamictization), volume expansion and associated cracking, and increased leachability. Natural mineral studies of zirconolite and perovskite show metamictization beginning about 10^{18} to 10^{19} α/cm^3 (projected exposure for one million years of repository storage), and volume increases of 2 to 3%, but no significant increase in uranium leach rates.[4]

4.3 CERAMIC WASTE FORM PROCESSING

A potential production process for manufacturing a ceramic waste form in the DWPF was defined in the alternative forms processability study.[10] A schematic diagram of major steps in the process is shown in Figure 4-1. This process is considerably more complex than the reference glass process (Section 3.2.3) and would require a larger and more expensive processing facility.

TABLE 4-5

Mechanical Properties of Synroc-D[2]

Property	Synroc-D
Tensile Strength, MPa	75.9*
Compressive Strength, MPa	280
Young's Modulus, GPa	139
Poisson's Ratio	0.28
Density, g/cm^3	4.0
Fraction of Fines Generated in Impact of 10 J/cm^3,** %	0.16

* For Synroc-C (Synroc formulation for simulated commercial power reactor waste).

** Reference 9. Fraction of particles less than 10 micrometers in size.

TABLE 4-6

Thermal Properties of Synroc-D[1]

Property	Synroc-D
Thermal Conductivity, W/m•K	1.85 (20°C) 1.91 (200°C)
Heat Capacity, J/g•K	0.74 (20°C)
Thermal Diffusivity,* m^2/s	6.5×10^{-7}
Linear Thermal Expansion Coefficient, K^{-1}	11×10^{-6}**
Solidus Temperature, °C	1270

* Calculated from other properties.

** For 22 to 950°C.

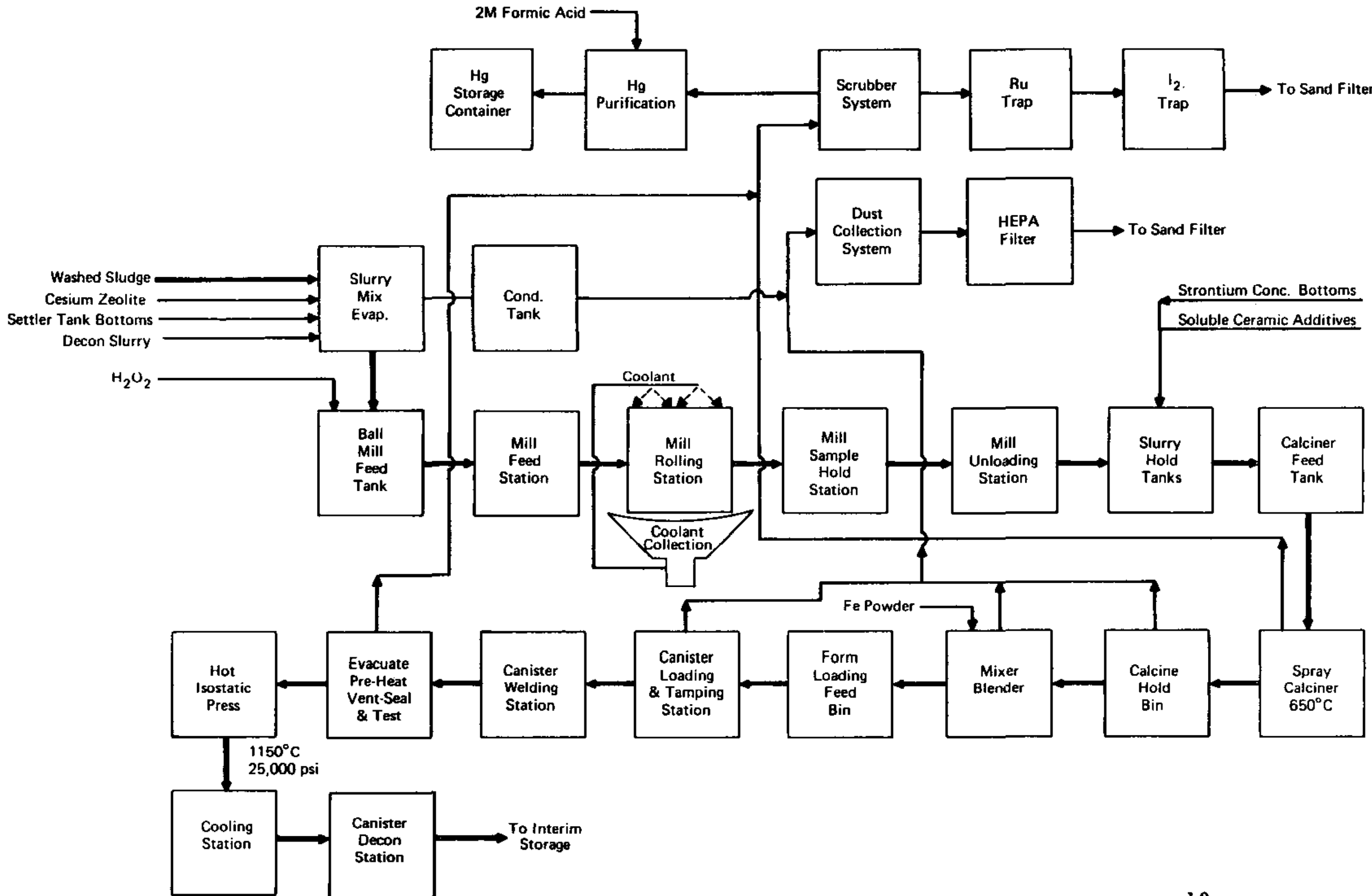

FIGURE 4-1. Crystalline Ceramics Process Flowsheet[10]

The ceramic process starts with essentially the same waste feed streams as does the reference borosilicate glass process except that aluminum is retained in the sludge feed. Washed sludge is combined with process recycle streams and cesium-loaded zeolite from supernate processing and concentrated to 40 wt % solids. The concentrated slurry is ball milled to reduce particle sizes in the feed. The milled slurry is mixed with the small amount of strontium removed from the supernate and with chemicals added to achieve the desired composition. The mixture is then spray calcined at 650°C. The calcined powder is blended with iron powder (to control cation oxidation states during consolidation), loaded into carbon steel canisters, and tamped to 50% theoretical density.

The canister is heated under vacuum to 800°C to eliminate residual volatiles, sealed, and placed in a hot isostatic press (HIP). In the HIP, the canister and its contents are isostatically pressed in argon at 170 MPa pressure and 1150°C. At this temperature and pressure, the volume of the canister decreases by 50%, and the density of the ceramic approaches the theoretical density of 4.0 g/cm^3. Formation of the desired phases occurs simultaneously with the reduction of porosity. Three carbon steel canisters, 0.56 m in diameter by 0.91 m high, are stacked inside a stainless steel canister, 0.61 m in diameter by 3.0 m high (dimensionally the same as the reference borosilicate glass canister). The waste canister is sealed by welding, decontaminated, and then transferred to an interim storage facility until a geologic repository becomes available.

4.4 DEVELOPMENT REQUIREMENTS AND GOALS

Extensive laboratory tests have been performed to develop and characterize the Synroc-D form with simulated SRP waste,[2,5] and a process for producing the ceramic has been demonstrated on a laboratory scale.[5] A potential production process has been defined, and from it a conceptual design of a ceramic waste form processing facility was developed.[10] Future development efforts would involve: (1) scale-up and demonstration of process equipment, unit operation tests, and integrated process tests; and (2) optimization of the ceramic form's phase chemistry.

Equipment development requirements identified for the ceramic process are extensive and include:[10] a vacuum ball mill suitable for remote operations, a modified remotely operated pipe connector with special provisions for evacuating and sealing containers, a sampling system for slurry particle size determination, a calciner atomization system, a monitoring system for calciner skin temperature, a fluid energy mill for calcine pickup, an in-can tamper, a remote HIP, and a canister resistant to nonuniform collapse. In general, these needs will require invention and extensive development. Other process-related areas requiring development include process control methods and techniques to minimize dusting. Product development requirements include: hot cell testing to demonstrate that a high-quality ceramic form can be made with actual waste, and actinide doping studies to demonstrate the effects of self-irradiation on the long-term stability of Synroc-D.

Optimization studies could lead to product and process improvements in the following areas:[2,5,10,11]

- Optimizing the phase chemistry to decrease leachability of cesium and strontium from silicate phases. Both LLNL and Rockwell Science Center have shown that improvement in leach resistance of up to a factor of 10 for strontium is possible.

- Demonstrating that selectively milling only the larger particles in the sludge feed (thereby reducing the size and cost of ball milling) does not affect adversely subsequent phase formation and radwaste partitioning during consolidation.

- Optimizing the calcination step to improve reliability. Fluidized bed as well as spray calciners merit consideration.

- Optimizing the hot consolidation step to improve product quality and process flexibility.

4.5 ENVIRONMENTAL CONSEQUENCES

4.5.1 Preparation, Interim Storage, Transportation, and Repository Operations

The environmental effects of immobilizing SRP high-level waste in Synroc-D, storing the ceramic waste canisters at the DWPF until a geologic repository becomes available, transporting the waste canisters to the geologic repository, and operating the repository would be very small and similar to impacts projected for the borosilicate glass waste form (Sections 3.4.1 and 3.4.2).[12,13] Minor differences would result from a larger DWPF required for the ceramic form and from a smaller number of ceramic canisters to be shipped and emplaced in the repository, but these differences would not affect ability to operate within applicable regulations. Overall risks from release of radioactivity to the environment from extreme transportation accidents, from repository operations or from long-term isolation are proportional to the total quantity of high-level waste transported to and emplaced in the repository and would be approximately the same for the ceramic and the glass waste form.

4.5.2 Long-Term Effects of Isolation

Like borosilicate glass, Synroc-D would be a suitable waste form for long-term isolation of SRP waste. No phenomena have been observed that would significantly degrade the ceramic's ability to limit radionuclide release from a repository. Although no long-term leaching data or data for forms containing actual waste exist, MCC tests have shown uranium leach rates in particular to be very low for Synroc (Section 4.2.1). Under expected repository conditions, actinides with low solubilities might be released at an even lower rate.

As discussed in Section 3.4.3, release rates in this range would yield negligibly small doses.

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